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Book review

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Molecular Thermodynamics.
University Science Books, Sausalito, California.
656 pages, £42.95
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This book, as the title suggests, presents thermodynamics from the molecular view, with continuing reference to the electronic energy states and partition functions of the molecules in gases and condensed states. It is an extremely well designed text for the second or third-year student in physics or chemistry who has had some background in particle physics and chemical bonding and is now ready to use that background to understand the atomic nature of enthalpy, entropy and free energy. The text progresses logically from a review of fundamentals to a detailed explanation of deviations from simple concepts based on molecular structures.

The first four chapters (pp. 1–184) are an excellent introduction to the molecular view of thermodynamics. Chapter 1 reviews the concepts of energy levels and degeneracy with models of simple atomic and molecular systems. It demonstrates nicely how quickly a system can become complex at the atomic and subatomic level. In Chapter 2, this information is then applied to both ideal and real gases. The uses and limitations of the van der Waals, Redlich Kwong and Peng-Robinson equations are detailed as well as the use of the compressibility factor and virial expansion coefficients. The third chapter gives considerable detail on the derivation of the Boltzmann factor and calculation of the partition function for systems such as a proton in a magnetic field, a monatomic gas and an atomic crystal. The relationship of energy and specific heat to the partition function is also derived. This theme is carried forward to Chapter 4 where the translation, rotation, vibration and electronic contributions to the partition function of ideal gases are explored in detail with comparison between calculated and measured values.

Chapters 5 through 7 (pp. 185–300) deal with the three laws of thermodynamics. There is a solid introduction to the first law with a good description of work, reversible work and maximum work. Enthalpy is introduced and a clear distinction between path and state functions is made. The second law is well described, both from a macroscopic and molecular view. Entropy of mixing, entropy of expansion and irreversible reactions are explained. There is an excellent and easily understood chapter on entropy at zero K. The discussion of entropy in terms of molecular quantum states is particularly well done as is also the use of standard entropies to calculate entropy change.

Chapters 8 and 9 (pp. 301–386) closely follow the format found in various other texts on chemical thermodynamics. They deal with Helmholtz and Gibbs energies and with phase equilibria. Free energy is introduced and related to reversible work. A good description of fugacity and standard states for gases is accompanied by a useful look at Maxwell's relations. The phase rule and phase diagrams for single component systems are covered in some detail with good use of free energy versus temperature diagrams. The evaluation of chemical potential using partition functions is detailed.

Solution theory is covered in two chapters (pp. 387–476), one on liquid–liquid solutions and one on liquid–solid. These provide solid coverage of partial molar properties, ideal and regular solutions, the Gibbs-Duhem equation, Raoult's and Henry's Laws, alternate standard states and activities. The reader is introduced to activities based on mole fraction, molarity, and molality and the relations among them. This sections ends with a description of various colligative properties for electrolytes and non-electrolytes along with various uses of the Debye–Hückel theory.

Chapters 12 and 13 (pp. 477–580) deal with chemical equilibrium and the thermodynamics of electrochemical cells. The former is very useful in outlining how to use thermodynamics to solve problems. The latter is a very workmanlike description of what one has to know to understand cells and half-cells, batteries and fuel cells. The section on liquid junction potentials is particularly well done.

The book concludes with a chapter (pp. 581–638) on non-equilibrium thermodynamics. This is an interesting read on how entropy increases in nonequilibrium systems and the role of fluxes and forces. However, although it may whet the appetite, it is not an essential part of the text.

A real strength of the text is the example problems which are solved throughout each chapter and the collection of 40 to 60 problems for the student at the end of each chapter. These are well chosen examples of the application of the theories and formulas derived throughout the book. There are two "added extras" that this reviewer found particularly worth while. At the end of the first five chapters, there are "Math. Chapters" which review key mathematical concepts used in the book including Numerical Methods, Probability and Statistics, Series and Limits, Partial Differentiation, and the Binomial Distribution and Stirling's Approximation. These five sub-chapters are very well explained and are a very real help in understanding the derivations and problems that occur throughout the text. The second feature is a brief biography and photo at the start of each chapter that shows that Planck, van der Waals, Boltzmann, Lewis, Onsager, etc. were very real people who led very interesting lives.

In summary, this is a well-written book that will serve as a bookshelf classic for the student learning thermodynamics for use in chemistry or physics. At £42.95 it is highly recommended.

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